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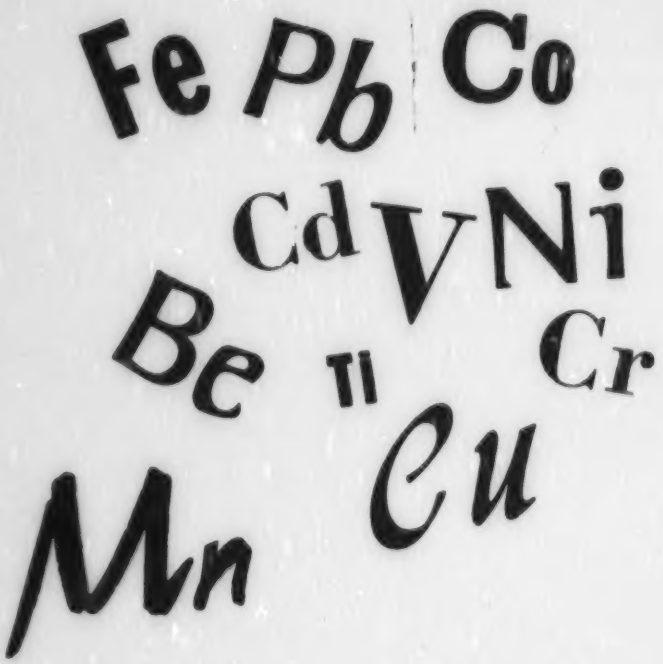

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
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16. ABSTRACT

This report examines trends over the past 10 years (1965-74) in ambient concentrations for 11 metals: beryllium, cadmium, chromium, copper, cobalt, iron, lead, manganese, nickel, titanium, and vanadium. The trends are derived from samples collected from 92 urban and 16 nonurban hi-vol stations in the National Air Surveillance Network. For purposes of presentation, the trace metals were grouped into two broad categories: the metals related to fuel combustion and those related to industry. Possible reasons for the trends observed are given for most of the metals studied.

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Beryllium	Vanadium		
Cadmium	National Air Surveillance Network		
Chromium			
Copper			
Cobalt	Manganese		
Iron	Nickel		
Lead			

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NATIONAL TRENDS IN TRACE METALS IN AMBIENT AIR 1965 - 1974

by

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1. INTRODUCTION AND OVERVIEW

Airborne concentrations of metals are a concern for three reasons: They are generally associated with particles in the respirable size range, many possess known toxic properties,[1] and they can act as catalysts in atmospheric reactions such as the conversion of sulfur dioxide to sulfates. This report examines trends over the past 10 years in ambient concentrations for 11 metals: beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), cobalt (Co), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), titanium (Ti), and vanadium (V). The trends are derived from samples collected from 92 urban and 16 nonurban hi-vol stations in the National Air Surveillance Network (NASN). All samples were analyzed at the central NASN laboratory, now part of EPA's Environmental Monitoring and Support Laboratory. Because of limitations inherent in these data, the results are intended primarily as a qualitative description of general patterns rather than as a precise quantitative analysis.

This report consists of four major sections: (1) a background section describing the data base and providing general information on emissions, (2) a section presenting the observed trends, (3) a section discussing the possible reasons for the trends, and (4) a concluding or summary section. The basic information is highlighted in three tables summarizing emissions, trends, and possible causes for the observed trends. For purposes of presentation, the trace metals have

been grouped into two broad categories: the metals related to fuel combustion--beryllium, lead, nickel, titanium, and vanadium--and those related to industry--cadmium, chromium, cobalt, copper, iron, and manganese.

The major findings of this investigation are as follows:

- In general, ambient metal concentrations have declined in most urban areas with the exception of copper, titanium, and possibly chromium.
- The downward trend in lead concentrations is due to the lower lead content of gasolines sold in recent years.
- The decline in vanadium and nickel concentrations, particularly in the Northeast sector of the United States, results from desulfurization of petroleum, which also removes these impurities.
- The absence of trends in copper may be at least partly due to copper contamination of the sample from the commutator of the hi-vol itself.
- The increase in titanium concentrations over the 10-year period may be caused by the increase in coal consumed by electric utilities.

2. BACKGROUND

2.1 Ambient Monitoring Data

Hi-vol filter samples from the NASN have been routinely analyzed for certain metals going back to the early 1960's. The years 1965-74

are covered in this report. Earlier NASN metals data are of such a sketchy nature that they are of no practical importance for trends purposes. As they become available, data for subsequent years will be analyzed in future reports.

The NASN network consists of individual monitoring stations located in urban and nonurban areas throughout the Nation. The urban sites are usually located in the center-city business area, while the nonurban sites are either in Federal or State parks. For the metal analysis, individual 24-hour samples taken throughout most of the 10-year period on a biweekly schedule were combined by quarter and then analyzed to obtain quarterly composite measurements at each site. The laboratory methodology, lower discrimination level (LDL), and other characteristics of the 1970-74 data are described in an EPA report.[2] For most metals the LDL values were generally higher in the first 5 years (1965-69) than the most recent 5 years (1970-74) by at least an order of magnitude. Composite values less than these limits were given the value of one half of these limits--for example, a beryllium urban annual average in which every quarterly composite value is less than the 1965-69 LDL of 0.0002 micrograms per cubic meter ($\mu g/m^3$) will be given a value of 0.0001 $\mu g/m^3$ for computational purposes. The 92 urban and 16 nonurban sites qualifying for trend analysis are given in the Appendix to this report, with a brief description of the sites and how they were selected.

The data on airborne concentrations of metals reported here, by the very nature of their collection and analysis, provide useful measures of relative rather than absolute concentrations across time, between seasons, or between geographical regions of the country. Throughout the 10-year period, basically the same sampling and analysis procedures were used on all data. However, there are some possibly important differences in the manner the samples were analyzed:

(1) Since 1970, the LDL for most metals have been reduced substantially. Consequently, the procedure is more sensitive for detection of background metal concentrations in the blank or unexposed filters. In the earlier years, of course, blank metal concentrations may not have been detected, and thus no adjustment was made in the final measured value because of the much larger LDL used. The effect of this refinement in the analytical technique on the reported values is not known.

(2) Either all or part of the data for 1965 may involve samples where the muffle furnace was used for ashing as opposed to the much lower temperature ashing procedure used in the other years. An analysis of metal concentration before and after this change concluded that it does not apparently affect the more volatile metals such as cadmium and lead, which are the most likely to be affected. Hence, these data are included in the analysis.

(3) Samples for the first 5 years were analyzed using an emission spectrometer, while those for the 5 most recent years were generated with an emission spectrograph.

(4) The data were analyzed at different times and even places since the laboratory was moved in 1970 from Cincinnati, Ohio, to Research Triangle Park, N.C.

(5) The NASN metals data for the most recent 5 years are thought to be more precise and internally consistent than the earlier data since these data were analyzed together as a group; furthermore, the newer data are the result of two separate determinations, using the same composite extract, rather than one as was done prior to 1970.

The high data recorded in 1969 for most of the metals cannot be explained. The high values were most pronounced in vanadium and cadmium. This finding was discussed with appropriate personnel in the Office of Research and Development, and they could offer no explanation.[3] Removal of the 1969 data would not alter our assessment of overall trends.

2.2 Major Metal Emission Sources

The three highest emission categories have been determined for 9 of the 11 metals studied (Table 1). The rankings are based on nationwide estimates of emissions for 1970--the most recent year available.[4-7] No estimates are available for cobalt or iron.

Of the metals studied, iron is the most abundant in the earth's crust and in the ambient air. It exists as an impurity in fuels, has wide use, and, therefore, has a pervasive potential for emissions. A significant portion of the iron collected likely comes from its corrosion and incineration.

TABLE 1. Three Highest Emission Categories for Metals Studied

Metal	1970 U.S. Emission Estimates[3-6] (Tons)	Highest	% of Total	2nd Highest	% of Total	3rd Highest	% of Total
Fuel-Combustion-Related Metals							
Beryllium	170	Coal combustion	88	Oil combustion	6	Metallurgical processing	3
Lead	230,000	Combustion of leaded gasoline	93	Secondary lead smelting	2	Solid waste disposal	1
Nickel	7,300	Oil combustion	83	Stainless steel reprocessing	7	Mining and processing	4
Titanium	88,000*	Coal combustion	83	Use as pigment	5	Pigment Production	5
Vanadium	20,000	Oil combustion	90	Coal combustion	9	Metallurgical processing	1
Industry-Related Metals							
Cadmium	2,200	Incineration of plated metal	46	Metallurgical processing	43	Incineration of radiators	6
Chromium	17,000	Ferrochromium production	68	Refractory production	10	Coal combustion	9
Copper	14,000**	Metallurgical processing	64	Iron and steel production	20	Coal combustion	7
Cobalt	Unknown						
Iron	Unknown						
Manganese	18,000	Manganese alloys processing	57	Case iron reprocessing	17	Coal combustion	11

*As TiO_2.

**1969 emissions.

Beryllium, lead, nickel, titanium, and vanadium are most likely to be present in urban areas because their emissions are associated with combustion of gasoline, coal, or oil. They are present as impurities or, in the case of lead, as an additive in gasoline.

The other metals (Cd, Co, Cr, Cu, Mn) are more closely associated with their use in making steel or other alloys or their fabrication into end products. Higher concentrations of these metals would be most likely in urban or nonurban areas near steel plants, smelting operations, or other plants associated with the metals industry. Although many of the NASN sites are in areas not directly associated with major metal industries, several steel-producing centers, such as Pittsburgh, Pa.; East Chicago, Ind.; Ashland, Ky.; and Bethlehem, Pa., are represented in our set of trend sites.

3. TRENDS IN METALS

In the appraisal of trends, the 50th percentile (the median) and the 90th percentile of the annual averages were chosen as the statistics to best describe the change in metals concentrations over time. This was done to minimize the influence of individual extreme values and to simplify the characterization of trends for metals having large amounts of data below the detection limit. Also, these statistics can portray different aspects of the yearly average distribution--the 50th percentile, the typical, and the 90th, the high concentration site. Rigorous statistical techniques such as time series or regression analysis were not used because this degree of sophistication was

neither necessary nor advisable in light of the uncertainties present in the data. Instead, our presentation will rely heavily on graphical displays of the two percentile values and a subjective interpretation of these patterns.

3.1 Urban Trends

Figures 1 and 2 graphically present the urban metal concentrations (1965-74) for the two broad emission categories (combustion and industry) in terms of the 50th percentile of annual averages. The 90th percentile plots are not shown since they provided very similar results. Beryllium and cobalt are omitted because both the 50th percentile and 90th percentile values fall below the lower detection limit for all 10 years.

Trends in these metals are mixed over the 10-year period. For example, lead, iron, copper, and chromium do not show a discernible trend over the 10-year period, although both lead and iron show a downward trend over the past 5 or so years. Cadmium, manganese, nickel, and vanadium all shown downward trends over the 10-year period and, with the exception of cadmium, over the most recent 5 years as well. Titanium shows an increasing trend for the first 5 years and a stable pattern over the last 5 years. These patterns describe the trends for the group or urban sites as a whole and characterize the vast majority of individual station trends.

The percent of changes for the 11 metals and total suspended particulates were examined for the 10-year period and for the most recent 5-year period (Table 2). These figures are based on a comparison of averages for

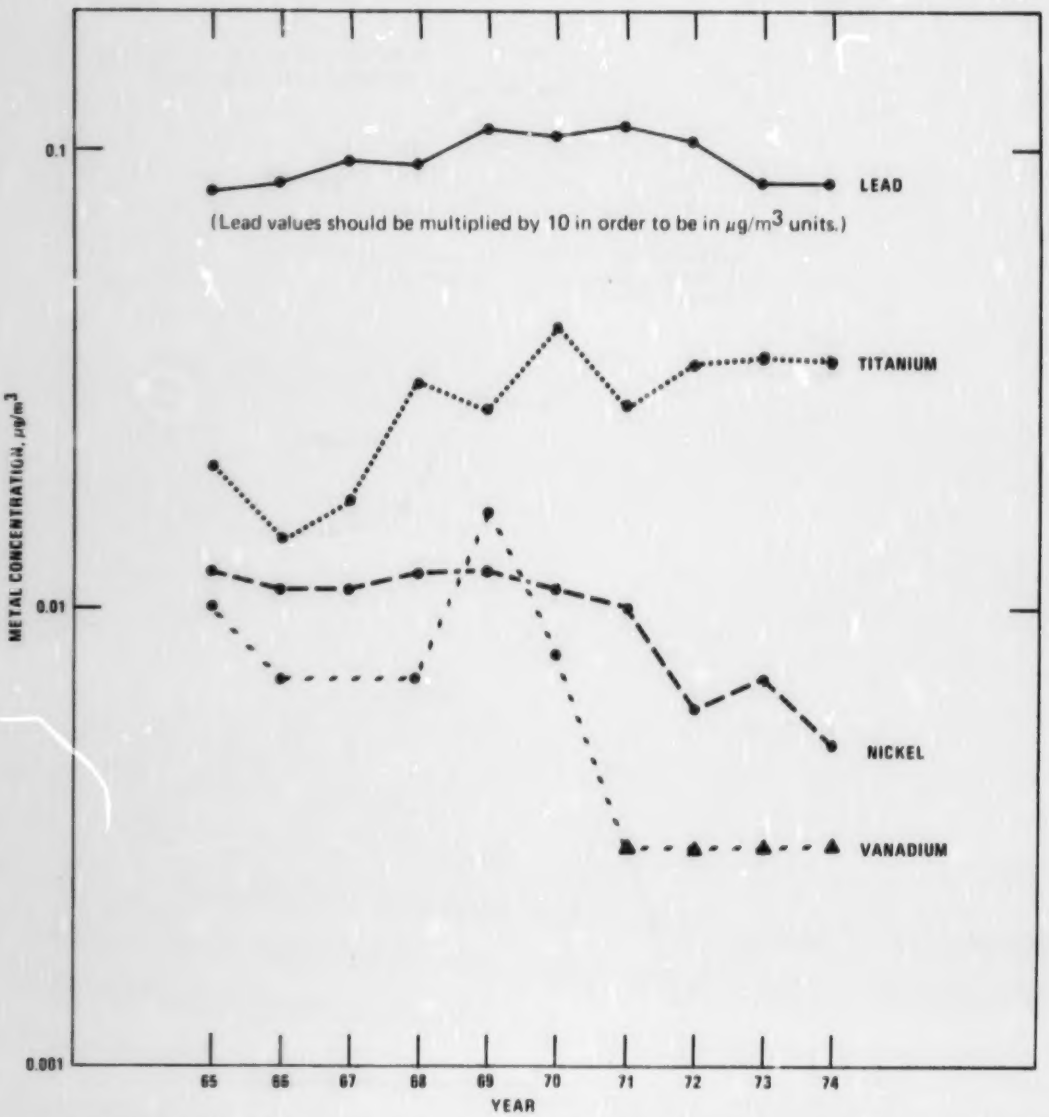


Figure 1. Trends in the 50th percentile at urban sites of annual averages for metals associated with primarily fuel combustion sources. (▲ indicates value below lower discrimination limit.)

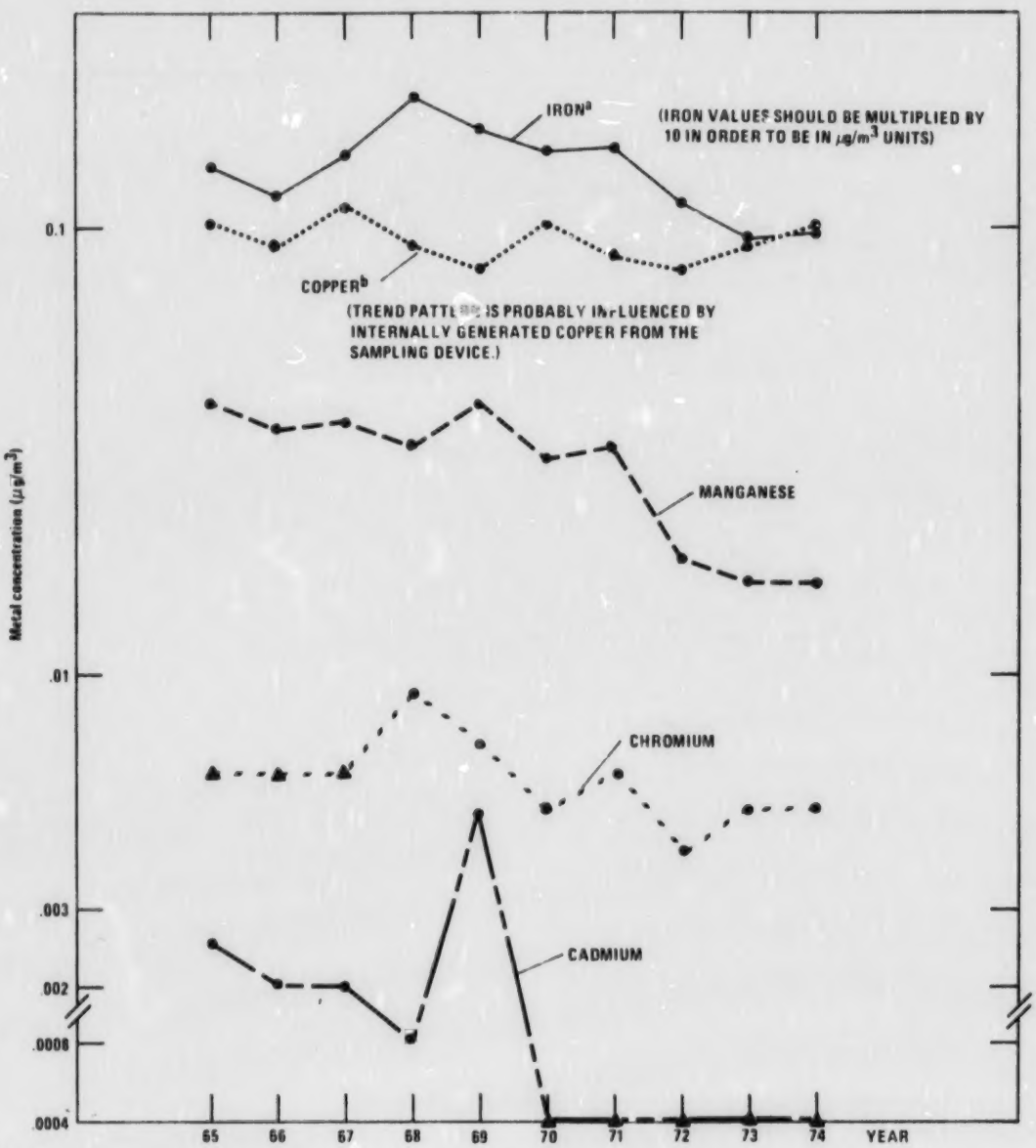


Figure 2. Trends in 50th percentile of annual averages for metals associated with metal industry sources at urban sites. (▲ indicates value below lower discrimination limit.)

TABLE 2. Percent Change in 50th and 90th Composite Statistics for Urban Sites

Metal	1965-1974 1965-67 vs. 1972-74 % change		1970-1974 1970-71 vs. 1973-74 % change	
	50 percentile	90 percentile	50 percentile	90 percentile
Fuel-Combustion-Related Metals				
Beryllium	Unknown*	Unknown*	Unknown*	Unknown*
Lead	+5	-5	-23	-10
Nickel	-40	-32	-40	-43
Titanium	+106	+22	0	-7
Vanadium	(-)**	-43	(-)**	-59
Industry-Related Metals				
Cadmium	(-)**	-57	Unknown*	-44
Chromium	(no change)**	-17	0	-12
Copper	-10	+3	+11	+8
Cobalt	Unknown*	Unknown*	Unknown*	Unknown*
Iron	-29	-40	-35	-54
Manganese	-50	-60	-50	-50
TSP	-18	-17	-4	-13

*Change cannot be determined because concentrations are below the lower discrimination limit.

**Only the sign of the change is given when one of the two intervals used in the comparison is less than the LDL.

the 1965-67 versus 1972-74 periods for 10-year interval and 1970-71 versus 1973-74 for the 5-year interval. In the 10-year trends, only titanium shows positive changes in both the 50th and 90th percentile statistics. Chromium shows no change in the median value and a 17 percent decrease in the 90th percentile. Copper and lead percent changes lie mostly in the stable interval (-10 to +10 percent); the remainder (with the exception of beryllium and cobalt for which no trend can be determined) appear to have declined in ambient concentrations over this time period. Copper's stability appears to be an artifact caused by a contaimination problem from the hi-vol sampler.

Trends for the most recent 5-year period (1970-74) are similar with the exception of lead, which now shows a modest decline, and titanium and chromium, which exhibit more stable patterns. The median and 90th percentile TSP concentrations have declined 18 percent and 17 percent, respectively, over the 10-year period for these groups of sites. However, TSP concentrations have changed much less (-4 percent) over the most recent 5-year period in the typical or median concentration range. TSP concentrations at the high end of the concentration distribution, as characterized by the 90th percentile, continue to show a modest decline (-13 percent).

The urban trend in the ratio of metal to TSP was considered for iron, lead, and vanadium. Trends in the fraction paralleled the raw concentration trends almost exactly. This indicates that it is not just the declining trend in TSP that is causing the change in metal

concentrations, but it is a change over and above that expected from just collecting less TSP.

3.2 Nonurban Trends

Data from the nonurban stations were considered separately. Because of the lower levels and the smaller number of stations (16), detailed discussion is not warranted, and the conclusions must be treated as tenuous. However, data from the nonurban sites do indicate the following:

- Chromium, copper, lead, and titanium increased fairly steadily over the 10-year period
- Iron, manganese, nickel, and vanadium showed declines, especially during the 1970-74 period
- Beryllium, cadmium, and cobalt levels were below the LDL of the method.

4. POSSIBLE CAUSES FOR METAL TRENDS OBSERVED

4.1 Fuel-Combustion-Related Metals--Lead, Vanadium, Nickel, and Titanium

Of the four metals associated principally on a nationwide scale with fuel combustion sources, nickel and vanadium (which are both associated with oil combustion) show a substantial decline in concentration over the 10-year period, while titanium increased early in this period. Lead levels experienced an initial increase and then a decline.

4.1.1 Lead

The national composite 50th percentile of lead concentrations (Figure 1) increased from 1965 until 1971 and then declined from about 1.1 $\mu g/m^3$ to 0.84 $\mu g/m^3$--about a 24 percent decrease, with most of the decline occurring between 1972 and 1973. This general trend pattern is consistent at most sites studied. A recent report[8] of extensive lead data at urban locations in Los Angeles, Houston, Tulsa, and Chicago has shown a decreasing trend in particulate lead at each of these locations. Another site in DuPont, Wash., showed a decline in lead concentrations, while a distinctly rural site at Starke, Fla., showed a stable pattern. NASN lead concentrations are about 30 percent higher in the Far West (where the California sites predominate) and Northeast sectors than in the other three geographical areas of the country. This geographical difference in lead loadings must be due to the greater amount of gasoline consumed, particularly in the southern California and New York City areas. These results, however, should be used with caution owing to the relatively small number of stations in each area and the possible area differences in the impact of vehicular and other lead emissions at these monitoring sites. The NASN site located in downtown Los Angeles experienced the highest concentrations--averaging between 4 and 5 $\mu g/m^3$ until 1971 when the concentrations decreased to about 2 $\mu g/m^3$ in 1974. Nationwide, lead levels tend to peak during the winter months at most of the 92 urban sites, especially the California sites even though winter lead content levels in gasoline[9]

are generally lower in California and the rest of the country as well (Figure 3). This seasonal pattern in California has been at least partly explained there by the poorer overall dispersion of the atmosphere during the winter months.[10]

Since about the 1970 model year, automobiles have been built with lower compression engines--ones requiring lower octane gasoline and thus gasoline with lower lead content. As a result of this change, practically all new cars built since 1970 are able to use regular gasoline instead of the more leaded premium fuels. The result of the engine modification can be clearly seen in the lower lead content in gasoline[9] (both in regular and premium grades) after 1969 (Figure 4). Subsequently, sales of regular gas increased and sales of premium gasoline decreased. Lead contents in gasoline will continue to drop in the future because of the increasing use of no-lead gasolines in new cars equipped with catalytic converters. These factors, coupled with the consumption of a modest amount of low lead or no-lead gasolines introduced at about this same time, result in the modest (10 to 20 percent) decrease in ambient lead concentrations over this period. These changes are more than enough to offset a general increase in gasoline consumed from 1970-74. However, this increase in gasoline consumed is probably not felt as greatly at these predominately center-city areas since they are generally already at or near vehicular saturation. There may even have been a reduction in vehicle miles traveled in downtown areas during this time because of car pooling, improved mass transit

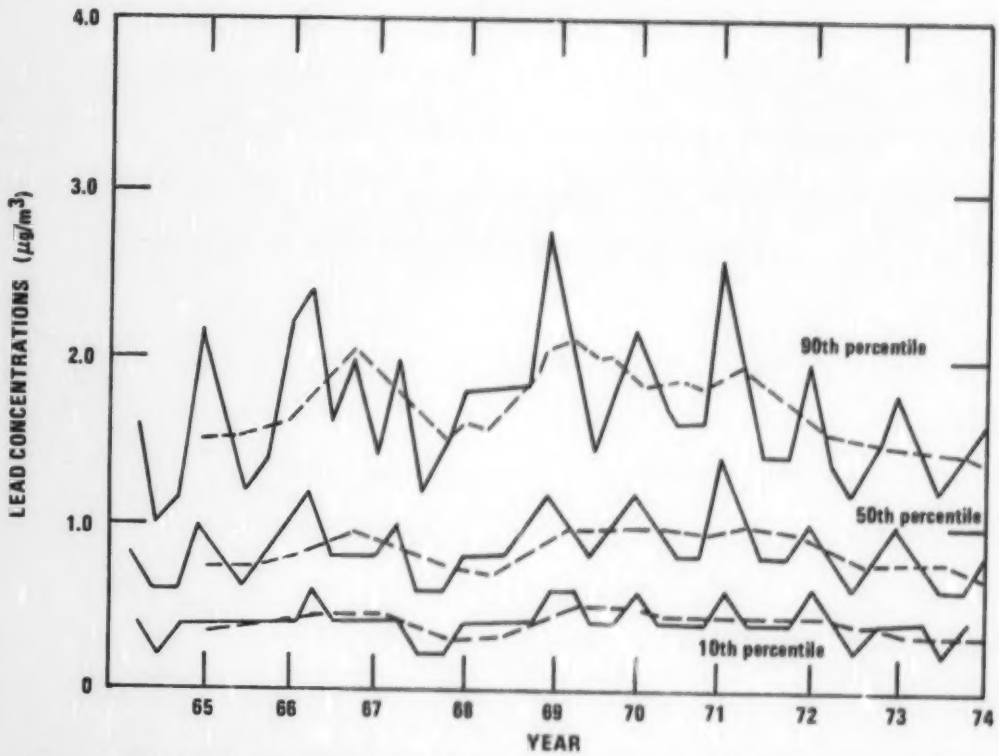


Figure 3. Seasonal patterns and trends in quarterly average urban lead concentrations.

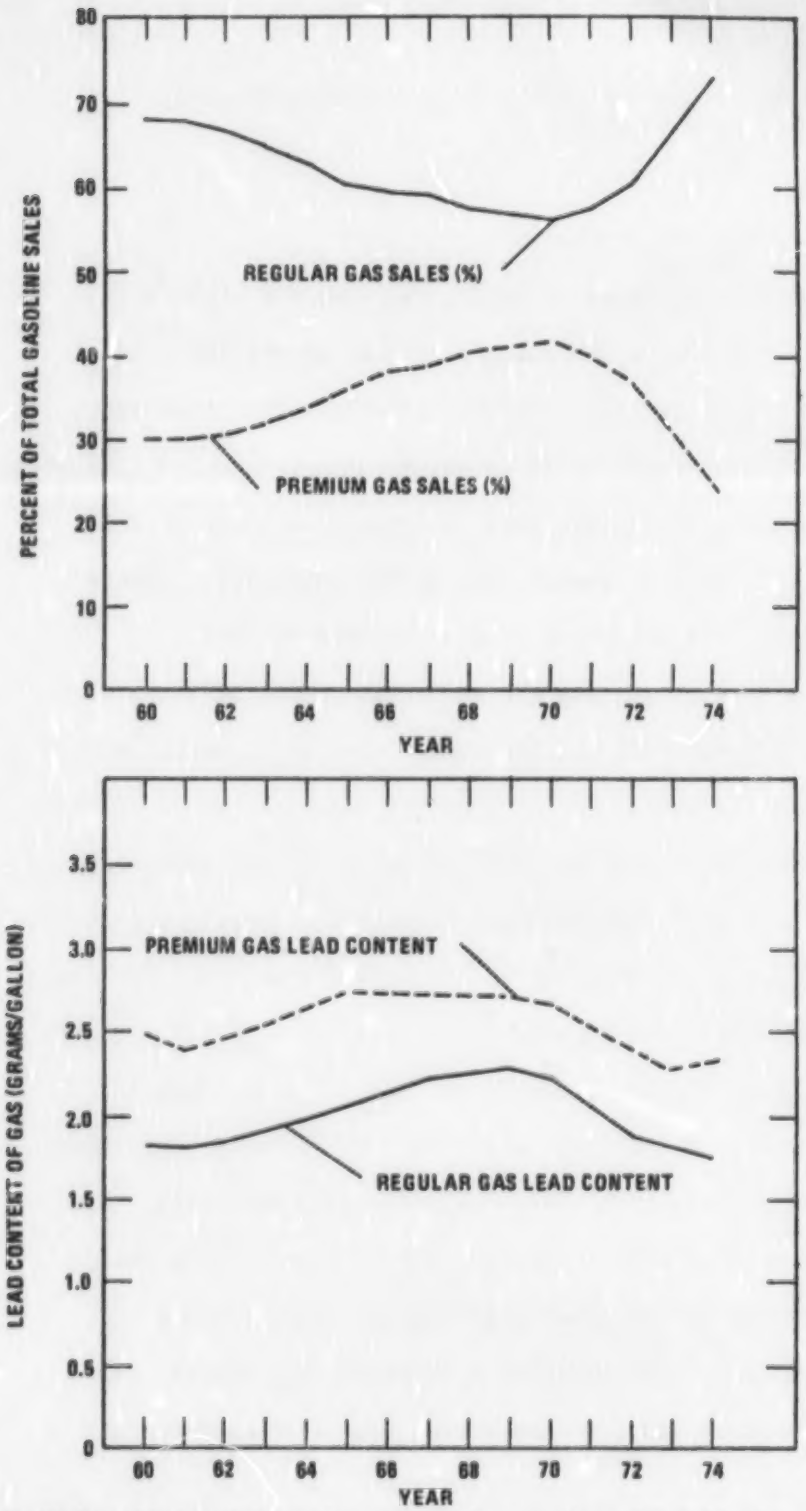


Figure 4. Nationwide trends in regular and premium gasoline sales and lead content, 1960-1974.

systems, and the loss of business activity to suburban shopping centers.

4.1.2 Vanadium and Nickel

The 50th percentile of vanadium annual averages for 1971-74 (Figure 1) falls in the LDL region and are assumed at the LDL value (0.003 $\mu g/m^3$), even though there are slight variations for these years below this limit. The abrupt rise in vanadium concentration in 1969 is puzzling and may suggest a positive bias in these data since most of the sites record their highest annual average for this year. However, the nonurban sites fail to show this unusual pattern in 1969.

Figure 5 shows five broad geographical areas of the United States. On the basis of 90th percentiles of the annual averages, vanadium concentrations in the Northeast are much higher over the entire 10-year period than the other regions (Figure 6). Once again, the 1969 value appears peculiar for most of the regional summaries, although the abrupt peak does not show up in the Northeast. Concentrations in the Northeast decreased 74 percent from 1969 to 1974 (0.35 $\mu g/m^3$ to 0.09 $\mu g/m^3$), with most of this drop occurring between 1971 and 1972. The changes in vanadium concentrations in the South are caused mainly by two or three stations showing relatively high readings in the 1972-74 period. This does not appear to be a pattern characteristic of sites in the region. Similar regional trends and regional gradients in concentrations are observed also for nickel. Nickel shows a fairly steady decline over the 10-year period. Both vanadium and nickel show a pronounced and

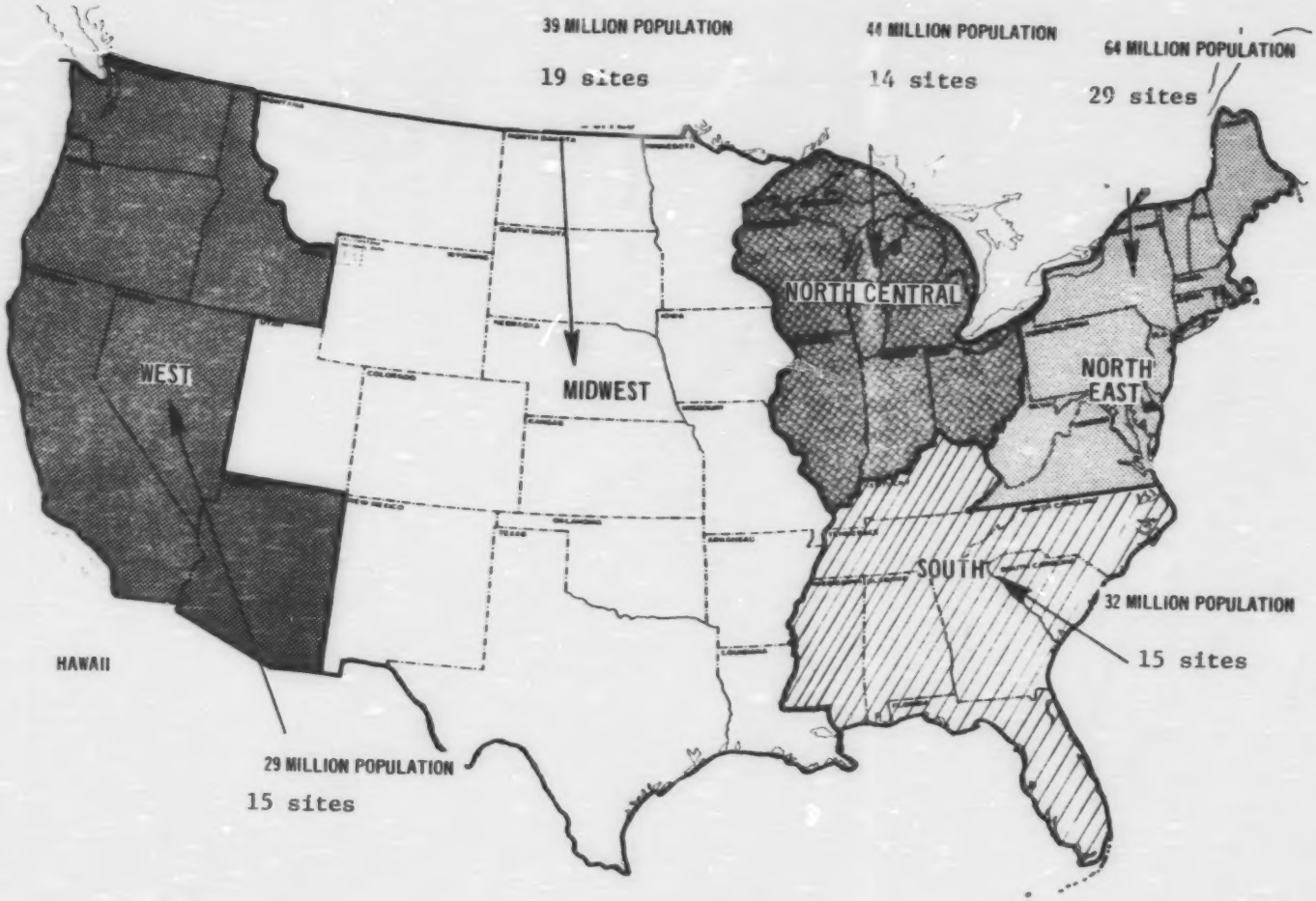


Figure 5. Five geographical areas of the country used in urban metal summaries

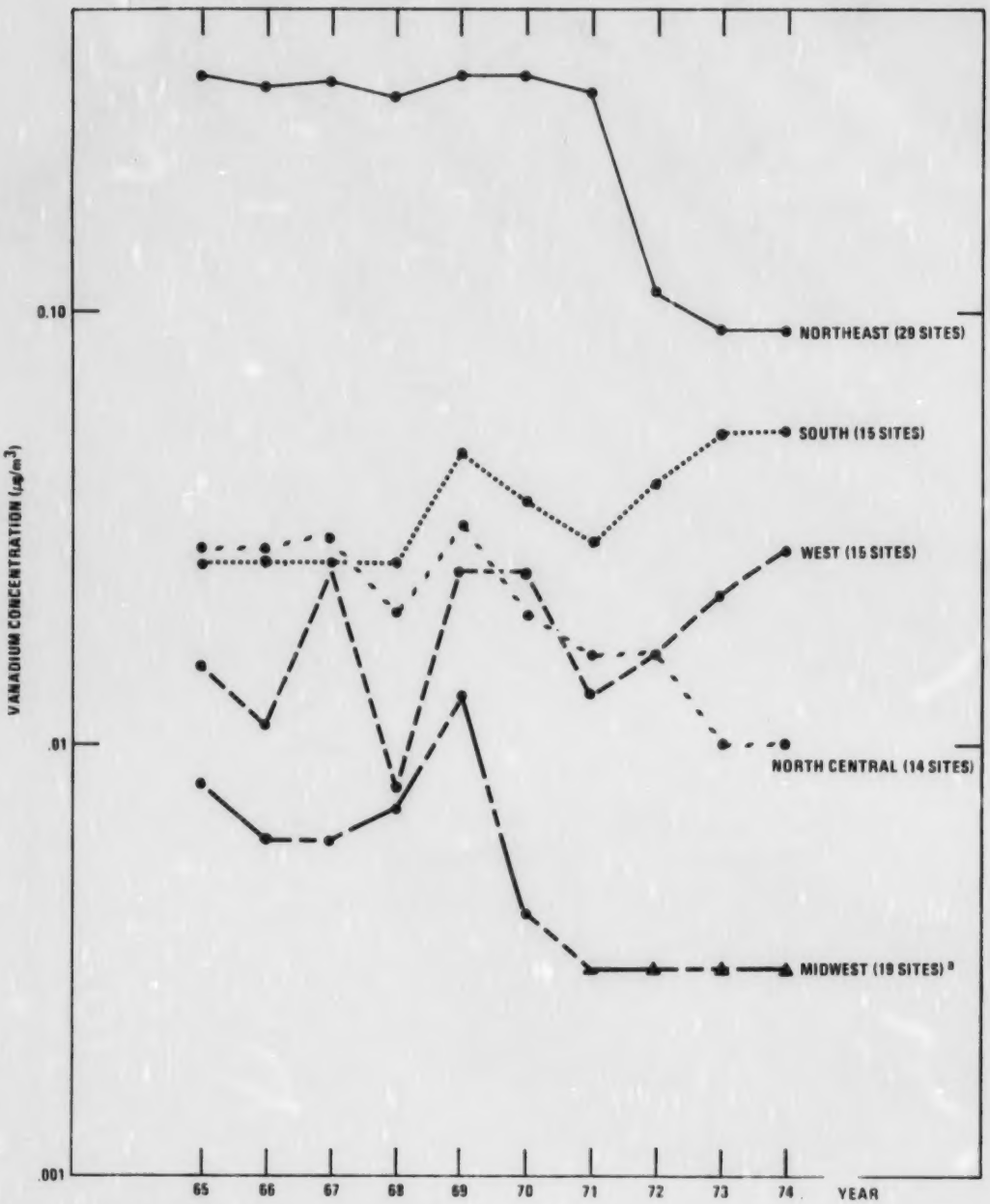


Figure 6. Regional trends in the 90th percentile of the annual averages for vanadium. (▲indicates value below lower discrimination limit.)

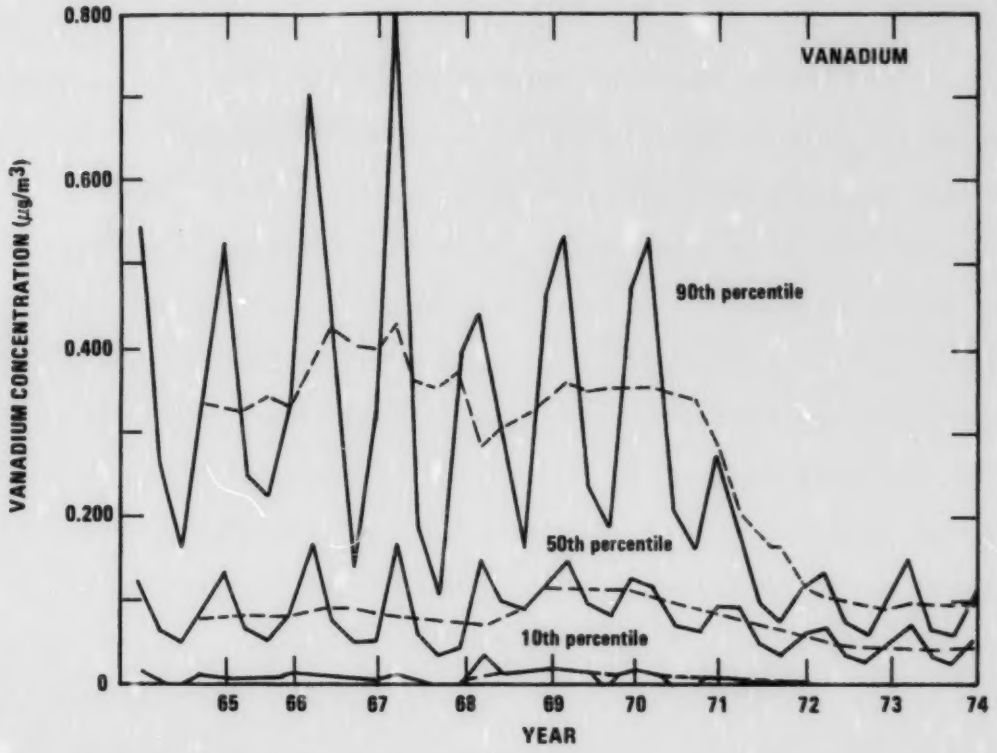
[a]1971-74 90th percentile below lower discrimination limit - 0.003 $\mu g/m^3$.

regular high winter-low summer seasonal variation in the 50th and 90th percentile in the Northeast (Figure 7). This is attributed to space heating emissions and poorer atmospheric dispersion in the winter.

This decline in vanadium and nickel concentrations, particularly in the Northeast, is attributed to the sulfur regulations that went into effect during this time.[11] Removal of sulfur from residual oil also indirectly removes vanadium and nickel, which are present in very high concentrations (~200 ppm for vanadium and about 20 ppm for nickel) in South American petroleum.[12] South American or Venezuelian petroleum is imported almost exclusively in the New York and northeastern seaboard areas. As an example, in New York City and the neighboring counties of Westchester, Suffolk, Rockland, and Nassau, sulfur regulations have reduced the maximum allowable sulfur in residual oil from about 1 percent in the 1968-1969 period to about 0.3 percent in 1973--a decrease of 70 percent. This percent change agrees very well with the percent change in vanadium concentrations (70 to 80 percent) over this same time at the New York City NASN site and with the percent change in vanadium in the composite 90th percentile for the Northeast region.

4.1.3 Titanium

Titanium concentrations have been increasing over the 10-year period (Figure 1), with 65 of 92 sites showing this pattern. Titanium concentrations are highest for the western stations, where the 50th percentile shows an increase from 0.045 $\mu g/m^3$ in 1965 to 0.058 $\mu g/m^3$ in 1974. The apparent upward trend may be the result of the 50 percent



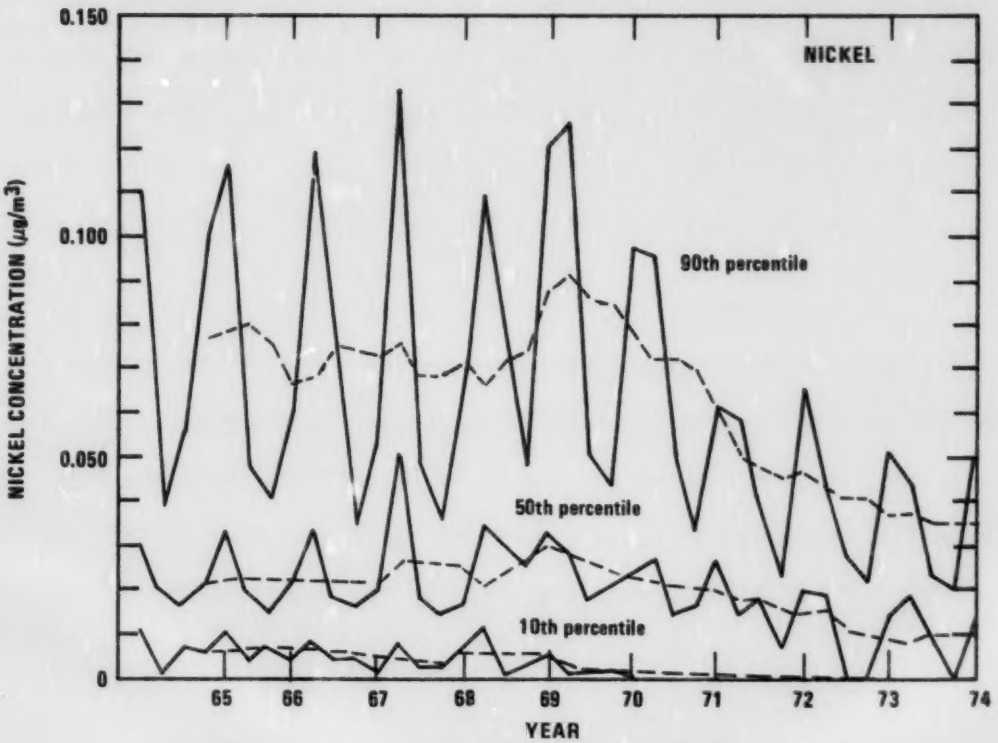


Figure 7. Seasonal variation in quarterly averages at urban sites in the northeast.

increase in consumption[13] of coal in electrical generating plants; coal combustion is the principal source of titanium, accounting for 83 percent of total TiO_2 emissions (Table 1).

4.2 Industry-Related Metals--Cadmium, Chromium, Copper, Iron, and Manganese

Copper and chromium show fairly stable patterns on the basis of 50th percentiles (Figure 2). Copper's very steady concentration pattern with time is rather surprising in light of the declining trends over the 10-year period shown by iron, manganese, and cadmium, other metals of this emission category group. It has been hypothesized, and there is persuasive supporting evidence, that copper contamination from wearing of the commutator on the motor of the hi-vol itself masks any possible trend.[14] Highest concentrations of iron, manganese, and cadmium are generally found in the North Central States and the Northeast where steel production is concentrated. The East Chicago, Ind., site recorded the highest iron concentration of any site studied, reaching its peak in 1969 of almost 10 $\mu g/m^3$; it then fell off to just over 4 $\mu g/m^3$ in 1974.

The decline in urban iron concentrations since 1968 has occurred at practically every site, including sites as different as Bethlehem, Pa., with a steel plant, and Durham, N.C., without one. The trend must be partially due to decreased iron emissions from other sources--for example, burning oil or gas instead of coal or improving incineration of refuse or other improved waste burning or waste removal practices. Declines in some steel producing areas, may be also due to particulate

controls at steel plants, although particulate controls in the steel industry as a whole have not been implemented extensively as yet. The downward trends of some other metals, such as cadmium and manganese, are more difficult to attribute to specific causes; it must be assumed that they were brought about by general particulate controls in processes emitting these elements. This apparent decrease occurred even though domestic production and consumption of cadmium and manganese stayed at about the same level throughout the period of interest.

5. SUMMARY AND CONCLUSIONS

In general, metal concentrations have declined in most urban areas with the exception of copper, titanium, and possibly chromium. Nickel, vanadium, iron, manganese, and cadmium show declines since the late 1960's, while lead concentrations began to drop in 1972. In contrast, titanium concentrations in recent years have remained at the same concentrations measured in the late 1960's. Chromium and especially copper were fairly constant throughout the 10-year period.

Table 3 summarizes metal trends and possible causes for these trends. Particularly in the cases of cadmium and manganese, the causes for the observed concentration patterns are more uncertain; however, they are given here to indicate plausible explanations. A cause for the inconsistent chromium pattern is not known. Trends in beryllium and cobalt could not be determined because of the very low concentrations. Trends in some of the metals studied have been correlated with known changes in emissions of these substances. Nationwide

TABLE 3. Trends in Urban Metal Concentrations and Their Possible Causes

Metal	Observed trends	Possible causes
Fuel-Combustion-Related Metals		
Beryllium	Unknown	--
Lead	Down last 5 years	Lower lead content in gasolines after 1969
Nickel	Down	Reduction of Ni in residual oils
Titanium	Up	Increasing use of coal in electric utilities
Vanadium	Down	Reduction of V in residual oils
Industry-Related Metals		
Cadmium	Down	Controls in metal industry and improved incineration practices
Chromium	No trend	Unknown
Cobalt	Unknown	--
Copper	No Trend	Contamination from hi-vol commutator
Iron	Down	Improved incineration or waste burning practices, fuel switching, controls in steel industry
Manganese	Down	Controls in metals industry

lead averages have declined because of the lower lead content of gasolines sold in recent years, primarily due to the introduction of lower compression engines around 1970. Vanadium, and nickel have dropped, particularly in the Northeast because the desulfurization of petroleum also removes these impurities. Titanium may have increased due to the rise in coal consumed by electric utilities. The absence of trends in copper may be at least partially explained by a contamination problem from the commutator of the hi-vol sampler. Decreasing iron, manganese, and cadmium concentrations are probably related to reduced particulate emissions from steel plants and related industries and from improved incineration and waste burning practices.

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7. REFERENCES

1. Lead (also Manganese, Chromium, and Vanadium). Committee on the Biologic Effects of Atmospheric Pollutants, Division of Medical Sciences, National Research Council, National Academy of Sciences, Washington, D.C. 1971, 1972, 1973, 1974.

2. Air Quality Data for Metals, 1970-1974, from the National Air Surveillance Networks. U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory, Research Triangle Park, N.C. 27711. July 1976.

3. Akland, Gerald. U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Research Triangle Park, N.C. 27711. Personal communications, August 1976.

4. Data file of Nationwide Emissions, 1970. U.S. Environmental Protection Agency, Office of Air Programs, Applied Technology Division, National Air Data Center. July 1972.

5. National Emissions Inventory of Sources and Emissions of Chromium, 1970. GCA Corp., GCA Technology Division, Bedford, Mass. 01730. Prepared for U.S. Environmental Protection Agency, Office of Air and Waste Management, Office of Air Quality Planning and Standards, Research Triangle Park, N.C. 27711. May 1973.

6. National Inventory of Sources and Emissions: Copper - 1969. W.E. Davis and Associates, 9726 Sagamore Rd., Leawood, Kans. Prepared for U.S. Environmental Protection Agency, Office of Air and Waste Management, Office of Air Quality Planning and Standards, Research Triangle Park, N.C. 27711. April 1972.

7. National Emissions Inventory of Sources and Emissions of Titanium. GCA Corp. GCA Technology Division, Bedford, Mass. 01730. Prepared for U.S. Environmental Protection Agency, Office of Air and Waste Management, Office of Air Quality Planning and Standards, Research Triangle Park, N.C. 27711. May 1973.

8. Trends in Air Lead Concentration. Petroleum Laboratory, E.I. DuPont De Nemours and Co., Inc., Wilmington, Del. 19898. July 26, 1976.

9. Motor Gasolines, U.S. Energy Research and Development Administration, Bartlesville Energy Research Center, Bartlesville, Okla.

10. California Air Quality Data, July-September 1973, Vol. V, No. 3. California Air Resources Board, Technical Services Division.

11. Monitoring and Air Quality Trends Report, 1972. U.S. Environmental Protection Agency, Office of Air and Waste Management, Office of Air Quality Planning and Standards, Monitoring and Data Analysis Division, Research Triangle Park, N.C. 27711. December 1973.

12. Vanadium. Committee on the Biologic Effects of Atmospheric Pollutants, Division of Medical Sciences, National Research Council, National Adacemy of Sciences, Washington, D.C. 1974.

13. Mineral Yearbook - Minerals Fuels, 1965-1974. U.S. Department of the Interior, Washington, D.C.

14. King, Robert B., and John Toma. Copper Emissions from a High-Volume Air Sampler. NASA Technical Memorandum, Lewis Research Center, Cleveland, Ohio 44135. March 1975.

15. Directory of Air Monitoring Sites, 1972. U.S. Environmental Protection Agency Office of Air Quality Planning and Standards, Monitoring and Data Analysis Division, Research Triangle Park, N.C. 27711. September 1973.

APPENDIX

Only NASN sites meeting a minimum amount and distribution of data in the period 1965-1974 were included in the trend analysis. In order to be included in the trend sample, a site had to meet the following criteria: (1) at least 2 years in the period 1965-69 had to be represented with at least three valid quarters and (2) at least 3 years in the period 1970-74 had to be represented with at least three valid quarters, with two of these years being 1970 or 1971 and 1973 or 1974. A valid quarter, which refers to the number of measurements submitted and not to the validity of the measurement, has at a minimum 5 days of data spread throughout the quarter. If one of the months in the quarter does not have any samples, then the other 2 months must have at least two samples apiece. Missing years of data were replaced by either interpolating from data on both sides of the gap or by simply using the preceeding or following annual average to replace missing annual average values at either end of the data record. A comparison of the results for sites having a complete year--that is, four valid quarters of data with that set having at least three quarters--did not reveal any important bias in the results.

The sites satisfying these basic requirements together with a brief description of the site[15] are given below:

City name	EPA Region	Site description
Gadsden, Alabama	IV	Center city-industrial
Huntsville, Alabama	IV	Center city-commercial
Mobile, Alabama	IV	*
Montgomery, Alabama	IV	Center city-commercial

City Name	EPA Region	Site Description
Anchorage, Alaska	X	Center city-commercial
Phoenix, Arizona	IX	*
Tucson, Arizona	IX	Center city-commercial
Little Rock, Arkansas	VI	Center city-commercial
West Memphis, Arkansas	VI	Center city-commercial
Glendale, California	IX	Center city-commercial
Long Beach, California	IX	Center city-commercial
Los Angeles, California	IX	Center city-industrial
Oakland, California	IX	Center city-industrial
Sacramento, California	IX	Center city-commercial
San Bernardino, California	IX	Center city-commercial
San Diego, California	IX	Center city-commercial
San Francisco, California	IX	Center city-commercial
Hartford, Connecticut	I	Center city-commercial
New Haven, Connecticut	I	Center city-commercial
Waterbury, Connecticut	I	Center city-industrial
Newark, Delaware	III	*
Jacksonville, Florida	IV	Center city-commercial
Tampa, Florida	IV	Center city-commercial
Atlanta, Georgia	IV	Center city-commercial
Honolulu, Hawaii	IX	Center city-commercial
Boise City, Idaho	X	Center city-commercial
Joliet, Illinois	V	Center city-commercial
Springfield, Illinois	V	Center city-commercial
East Chicago, Indiana	V	Suburban-commercial
Terre Haute, Indiana	V	Center city-commercial
Cedar Rapids, Iowa	VII	Center city-commercial
Davenport, Iowa	VII	Center city-commercial
Des Moines, Iowa	VII	Center city-commercial
Topeka, Kansas	VII	Center city-commercial
Wichita, Kansas	VII	Center city-commercial
Ashland, Kentucky	IV	Center city-commercial
Covington, Kentucky	IV	Center city-commercial
New Orleans, Louisiana	VI	Center city-commercial
Shreveport, Louisiana	VI	*
Baltimore, Maryland	III	Center city-commercial
Worchester, Massachusetts	I	Center city-commercial
Flint, Michigan	V	Center city-commercial
Grand Rapids, Michigan	V	Center city-commercial
Trenton, Michigan	V	Center City-commercial
Duluth, Minnesota	V	*
St. Paul, Minnesota	V	*
St. Louis, Missouri	VII	Center city-commercial
Omaha, Nebraska	VII	*
Reno, Nevada	IX	Suburban-commercial

City Name	EPA Region	Site Description
Concord, New Hampshire	I	Center city-residential
Bayonne, New Jersey	II	Suburban-commercial
Glassboro, New Jersey	II	Suburban-residential
Newark, New Jersey	II	Center city-commercial
Trenton, New Jersey	II	Center city-commercial
Albuquerque, New Mexico	VI	Rural-commercial
New York City, New York	II	Center city-residential
Charlotte, North Carolina	IV	Center city-commercial
Durham, North Carolina	IV	Center city-commercial
Bismarck, North Dakota	VIII	Center city-residential
Akron, Ohio	V	Rural-commercial
Youngstown, Ohio	V	Center city-industrial
Tulsa, Oklahoma	VI	Center city-residential
Allentown, Pennsylvania	III	Center city-commercial
Altoona, Pennsylvania	III	*
Bethlehem, Pennsylvania	III	Suburban-commercial
Harrisburg, Pennsylvania	III	Center city-commercial
Hazleton, Pennsylvania	III	Center city-residential
Pittsburgh, Pennsylvania	III	Center city-commercial
Reading, Pennsylvania	III	*
Scranton, Pennsylvania	III	Center city-commercial
Wilkes-Barre, Pennsylvania	III	Center city-commercial
York, Pennsylvania	III	*
Providence, Rhode Island	I	Center city-commercial
Columbia, South Carolina	IV	Center city-commercial
Greenville, South Carolina	IV	Center city-commercial
Memphis, Tennessee	IV	Center city-commercial
Nashville, Tennessee	IV	Center city-commercial
Dallas, Texas	VI	Center city-commercial
Houston, Texas	VI	Center city-commercial
San Antonio, Texas	VI	*
Ogden, Utah	VIII	Center city-commercial
Burlington, Vermont	I	Center city-commercial
Hampton, Virginia	III	Center city-commercial
Norfolk, Virginia	III	Center city-commercial
Portsmouth, Virginia	III	Center city-commercial
Roanoke, Virginia	III	Center city-commercial
Seattle, Washington	X	Center city-commercial
Charleston, West Virginia	III	Center city-commercial
Kenosha, Wisconsin	V	Center city-commercial
Madison, Wisconsin	V	Center city-commercial
Milwaukee, Wisconsin	V	Center city-commercial
Casper, Wyoming	VIII	Center city-commercial

Nonurban Name		
Grand Canyon Nat. Park, Arizona	IX	Remote
Montgomery Co., Arkansas	VI	Remote
Mesa Verde Nat. Park, Colorado	VIII	Remote
Butte Co., Idaho	X	Remote
Acadia Nat. Park, Maine	1	Remote
Jackson Co., Mississippi	IV	Remote
Thomas Co., Nebraska	VII	Remote
White Pine Co., Nevada	IX	Remote
Coos Co., New Hampshire	I	Rural
Jefferson Co., New York	II	Remote
Cherokee Co., Oklahoma	VI	*
Curry Co., Oregon	X	Remote
Black Hills Nat. For., South Dakota	VIII	Remote
Matagorda Co., Texas	VI	Remote
Orange Co., Vermont	I	Remote
Yellowstone Nat. Park, Wyoming	VIII	Rural

*Information not available from National Aerometric Data Bank.